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Complex hydrides as room-temperature solid electrolytes for rechargeable batteries

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Abstract A central goal in current battery research is to increase the safety and energy density of Li-ion batteries. Electrolytes nowadays typically consist of lithium salts dissolved in organic solvents. Solid electrolytes could facilitate safer batteries with higher capacities, as they are compatible with Li-metal anodes, prevent Li dendrite formation, and eliminate risks associated with flammable organic solvents. Less than 10 years ago, LiBH_4 was proposed as a solid-state electrolyte. It showed a high ionic conductivity, but only at elevated temperatures. Since then a range of other complex metal hydrides has been reported to show similar characteristics. Strategies have been developed to extend the high ionic conductivity of LiBH_4 down to room temperature by partial anion substitution or nanoconfinement. The present paper reviews the recent developments in complex metal hydrides as solid electrolytes, discussing in detail LiBH_4 , strategies towards for fast room-temperature ionic conductors, alternative

compounds, and first explorations of implementation of these electrolytes in all-solid-state batteries.

1 Introduction: the relevance of solid-state electrolytes

The electrolyte in present-day lithium-ion batteries, typically based on oxidic intercalation materials such as lithium cobalt oxide (LiCoO_2) cathodes and graphite intercalation anodes (Li_xC), usually consists of lithium salts dissolved in organic liquids. This enables fast Li^+ transport between the electrodes, but is associated inevitably with potential safety, stability, and cycle-life issues. Increasing the energy density is a major incentive for battery development and research. A factor of 2–3 in energy density should be gained to render the current driving range (of about 160 km) of all electric vehicles competitive to that of petrol-driven cars. Energy density becomes even more critical when considering also medium-scale applications, such as local load levelling of solar energy and wind power [1–4].

Using lighter electrode materials is crucial to attain higher energy densities (see Fig. 1). Li_xS is proposed as a next-generation cathode material, with as a major challenge the large volume change upon cycling and the solubility of polysulphides in organic solvents [5, 6]. The ultimate dream is a cathode reaction of Li with $\text{O}_2/\text{H}_2\text{O}$ (lithium-air batteries), with energy densities close to that of gasoline theoretically possible, but for which achieving full reversibility is a major issue to solve [7]. On the anode site, using conversion metal hydrides could lead to higher gravimetric densities [8–14]. Also, metallic lithium anodes have theoretical energy densities even ten times higher than current carbon-intercalation anodes. However, metallic

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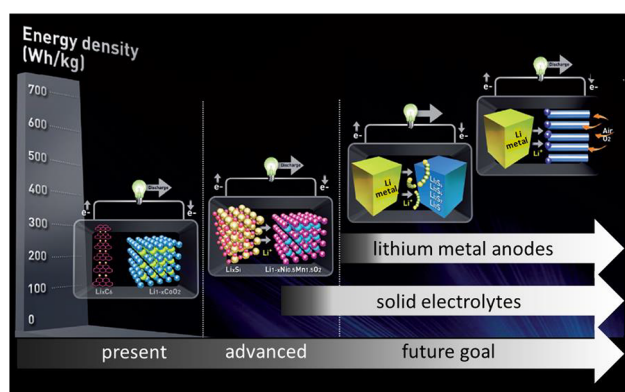


Fig. 1 Illustration of developments towards higher energy density lithium-ion batteries. Modified based on a figure in [2]

lithium is not thermodynamically stable in contact with any organic solvent, and commercialisation of batteries based on Li-metal anodes in combination with liquid electrolytes seems unlikely [2, 15, 16].

Solid electrolytes could offer compatibility with Li-metal anodes, prevent short-circuiting in sulphur-based batteries, and eliminate the safety risks associated with the flammability and volatility of organic solvents. However, it is a formidable challenge to identify a light-weight and low-cost solid material with sufficiently high ionic conductivity (at least 10^{-4} – 10^{-3} S cm $^{-1}$ at room temperature) which at the same time possesses a large electrochemical stability window and has negligible electronic conductivity. For thin film batteries in microdevices, so-called LISICON materials have been developed, of which Li₁₀GeP₂S₁₂ [17] seems one of the most promising ones, but large-scale application is hindered by the high cost of electrolyte fabrication and components. Several other multi-metal oxynitrides and titanates are being considered, but at present no material satisfying all requirements has been identified, and hence the search for new types of solid electrolytes is a very active field of research.

2 Complex metal hydrides as solid-state electrolytes

Complex metal hydrides are solids with an ionic lattice composed of metal cations and complex hydride anions in which the atoms are predominantly covalently bound. This family includes boron hydrides such as LiBH₄, Li₂B₁₂H₁₂, NaBH₄, and Mg(BH₄)₂, aluminium hydrides such as LiAlH₄ and Na₃AlH₆, and a wide range of other compounds. Several hydrides, such as LiAlH₄ and NaBH₄, are in wide use as reductants in organic synthesis. Due to their high hydrogen content, they are also considered promising reversible hydrogen storage materials [18–20]. Despite

early reports [21], investigation of their potential as solid-state electrolytes has only taken full flight with the pioneering work of the group of Orimo [22, 23].

Like many other boron hydrides, LiBH₄, consisting of Li⁺ cations and [BH₄][−] anions, can be found in different polymorphs, depending on pressure and temperature (see Fig. 2) [24–27]. The orthorhombic phase, which is the stable phase at room temperature, has a low ionic conductivity ($\sim 10^{-8}$ S cm $^{-1}$ at 30 °C). However, in 2007 it was reported by the group of Orimo that the hexagonal phase, which is stable at temperatures above 110 °C under atmospheric pressure, has a remarkable high ionic conductivity ($\sim 10^{-3}$ S cm $^{-1}$ at 120 °C) [23]. For actual application in batteries, high ionic conductivities at *room temperature* are required. Henceforth, the interesting question is whether the high ionic mobilities in LiBH₄ can be extended to room temperature or whether alternative complex hydrides having this property are available.

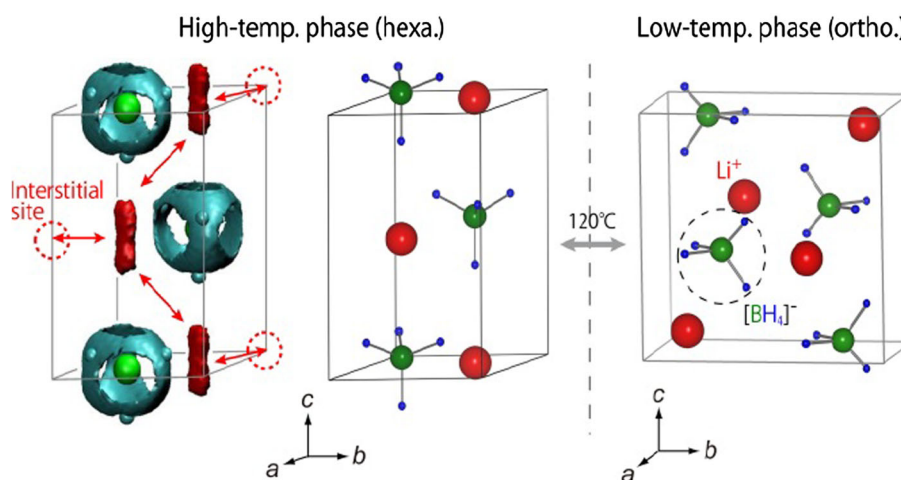
In this section, we start by briefly reviewing the findings on LiBH₄ as a fast-ionic conductor, and how the high conductivity behaviour was extended to room temperature by either partial anion replacement (Sect. 3) or the formation of a nanocomposite (Sect. 4). Subsequently, we will also discuss alternative complex metal hydrides with high ionic mobilities, and we will end with a brief conclusion and outlook. More details on complex metal hydrides as solid-state electrolytes can also be found in [28].

3 Fast room-temperature ionic conduction in LiBH₄ by partial anion substitution

Most notably Orimo and co-workers showed that replacing a fraction of the BH₄[−] anions by halide anions (I[−], Br[−] or Cl[−]) stabilises the hexagonal structure at lower temperatures and leads to high ionic mobilities persisting down to room temperature. They found the partial replacement of the [BH₄][−] anion with I[−] anions, especially effective. A single-phase solid solution was formed for a wide range of compositions up to 25–30 % of anion replacement. An ionic conductivity of 2×10^{-4} S cm $^{-1}$ at room temperature was obtained, and a minimum activation energy of 0.39 eV at a replacement of 13 % of the [BH₄][−] ions. Anion substitution stabilised the high-temperature phase to room temperature, but, as the solid solutions were obtained by ball milling, grain boundaries and defects also seem to play an important role [22, 29].

In the high-temperature phase, the Li⁺ ions are arranged in layers in the hexagonal plane, with probably two nearly equivalent Li⁺ sites. As in principle all sites are filled, the conduction is most likely related to Frenkel-pair defects (Li⁺ vacancies combined with interstitial Li⁺ sites).

Fig. 2 Crystal structures of the (right) low-temperature phase and (middle) high-temperature phase of LiBH_4 . (left) Isosurfaces of Li, B, and H populations obtained by first-principles molecular dynamics simulations [24]



Interstitial Li^+ can, with a relatively low activation barrier and probably helped by rotation of the neighbouring BH_4^- units, jump from one interstitial site to the next (see Fig. 2) [22, 24, 29, 30]. In the $\text{LiBH}_4\text{:LiI}$ solid solutions, the mobilities of Li^+ and $[\text{BH}_4]^-$ increase with increasing iodine content [30, 31]. Using mixed components was reported to make the system susceptible to phase segregation and reduced thermal and electrochemical stability [32, 33].

4 Fast room-temperature ionic conduction in $\text{LiBH}_4/\text{SiO}_2$ nanocomposites

Nanocomposites of light metal hydrides with high surface area carbon materials have been widely investigated for reversible hydrogen storage applications, as creating a large interfacial area between the hydrides and carbon scaffolds has been found to improve the kinetics and reversibility of hydrogen sorption and result in high hydrogen and $[\text{BH}_4]^-$ mobilities [34–36]. NMR suggested also high Li^+ mobilities in LiBH_4/C nanocomposites [35, 37], but carbon materials are electronically conductive, hampering detailed structural studies and ionic mobility measurements and their use as solid electrolytes.

Very recently, it was reported that nanocomposites of LiBH_4 with SiO_2 , prepared by melt infiltration under hydrogen pressure of ordered mesoporous SiO_2 scaffolds with LiBH_4 [38], displayed very high Li^+ conductivities ($10^{-4} \text{ S cm}^{-1}$) at room temperature (Fig. 3) [39]. These are surprisingly high values, given that these nanocomposites comprise a large fraction (up to 50 vol%) of insulating SiO_2 and also a significant void fraction. The high room-temperature ionic conductivity in LiBH_4 by confinement in a mesoporous SiO_2 matrix is stable (when

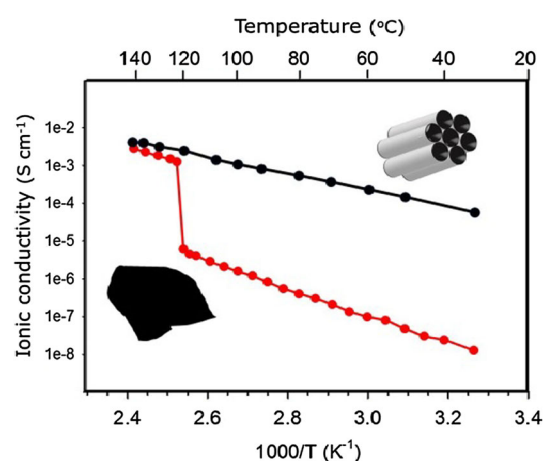


Fig. 3 Ionic conductivities of bulk and nanoconfined LiBH_4 . Macrocrystalline LiBH_4 displays high ion conductivities only in the high-temperature ($>110^\circ\text{C}$) polymorph. In contrast, the $\text{LiBH}_4/\text{SiO}_2$ nanocomposite shows high ionic conductivities even at room temperature [39]

temperature cycling to 140°C , electrochemically cycling $\pm 6 \text{ V}$) and reproducible [39].

The origin of the high ionic mobility in these nanocomposites is not yet well understood. Confinement of LiBH_4 in the oxide pores leads to limited stabilisation of the hexagonal high-temperature phase in the core of the pores. However, the high ionic mobility seems rather associated with the fraction of LiBH_4 that is close to the SiO_2 interface [39, 40]. In general high defect densities and low diffusion barriers are found at the interface between two solids, due to effects such as disorder, strain, and space charge regions. Also for other compounds, mostly studied as proton and oxygen conductors for fuel cells, the addition of oxide nanoparticles has been found to increase conductivity [41–43].

5 Other Li⁺-containing complex hydrides

Apart from LiBH₄, several other complex metal hydrides have been discovered to display fast conductivity. An interesting family is the system LiBH₄–LiNH₂–LiI. For instance, Li₂(–BH₄)(NH₂) and Li₄(BH₄)(NH₂)₃ show conductivities of 2×10^{-4} S cm^{−1} at 300 K. Also, lithium aluminium hydrides such as LiAlH₄ and Li₃AlH₆ are potentially interesting. Reported conductivities until now are relatively low (10^{-7} – 10^{-5} S cm^{−1} at 120 °C) [44], and they are better considered as anode materials [11, 45]. Another interesting class reported is the rare earth and chloride-containing materials from the LiRE(BH₄)₃Cl family (with RE=Ce, La, Gd), for which conductivities of up to 2×10^{-4} S cm^{−1} are reported at room temperature [46]. These examples highlight that the high ionic conductivities found in LiBH₄-based materials are by no means an exception, but in fact that high ionic conductivities are quite common in complex metal hydrides compounds, and hence, it is likely that many more potentially interesting materials will be synthesised and reported in the coming years. Having said that, existing literature also makes clear that moving towards increasingly complex materials, and increasing the number of elements and hence possible phases in the systems, makes it more and more a challenge to obtain phase-pure compounds, and is often not accompanied by a high stability upon cycling or temperature treatment.

6 Na⁺ superionic conductors

Due to fear of future lithium scarcity and hence high costs, also batteries based on other metals, such as Na⁺, Mg²⁺, and Al³⁺, are being intensively investigated as lower-cost alternatives, with especially Na⁺-based batteries attracting much attention [47]. As there are many similarities and trends across the family of complex metal hydride materials, a logical next step is to explore also compounds based on other alkali or alkaline earth cations. Orimo and co-workers found that Na₂(BH₄)(NH₂) obtained in the system NaBH₄–NaNH₂ shows a conductivity of 2×10^{-6} S cm^{−1} at 300 K [48]. Udovic and others reported in 2014 for the first time on the high ionic mobilities and conductivities for sodium borohydrides (Fig. 4). Interesting candidates are Na₂B₁₂H₁₂ (which exhibits a transition to high ionic conductivity at 205 °C) and Na₂B₁₀H₁₀ (which in pure form becomes conducting above ~100 °C) [49, 50].

7 Integration of these solid electrolytes into a battery

Optimising one component is not yielding a commercially viable battery, as compatibility with the other components in the system is crucial for real

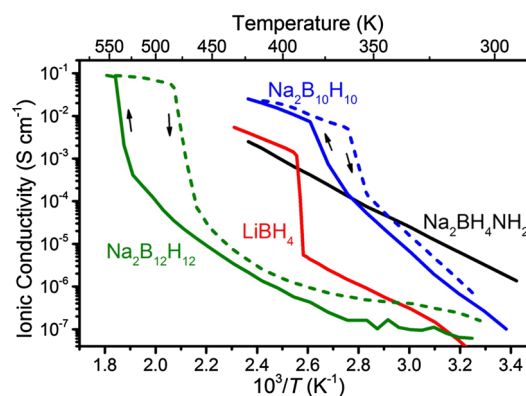


Fig. 4 Overview of some recently reported sodium boron hydrides showing interestingly high ionic conductivities [49, 50]. The conductivity of LiBH₄ is shown for comparison

application. Most efforts for the construction of all-solid-state batteries based on complex metal hydride electrolytes have been focussed on LiBH₄ [51–54]. LiBH₄ is stable in contact with metallic lithium, but its stability at the interface with the positive electrode, while facilitating fast and totally reversible exchange of Li⁺ ions with the electrode, is a challenge. First attempts were made with a LiCoO₂ electrode, intrinsically unstable in contact with LiBH₄ operated in the high-temperature phase (at 120 °C), but the stability and reversibility were much improved by applying a Li₃PO₄ coating between the LiCoO₂ and LiBH₄ [50]. Also TiS₂ was tested as a positive electrode [53], and the solid electrolyte was even combined with a metal hydride negative electrode [54]. More details on complex metal hydrides for bulk-type all-solid-batteries can be found in [28].

8 Conclusions and outlook

It is clear that for future-generation, higher-capacity, lithium-ion batteries, solid-state electrolytes are a crucial component. Complex metal hydrides, and specifically LiBH₄-based compounds, have recently been shown to be a promising class of fast-ionic conductors. Although intrinsically macrocrystalline LiBH₄ displays high conductivities only at temperatures above 110 °C, more recent strategies such as partial anion substitution and nanoconfinement have been developed that lead also to high conductivities at room temperature. Yet, LiBH₄ is not unique, and many other complex metal hydrides containing Li⁺ as well as Na⁺ and probably other cations also exhibit high ionic conductivities. It is evident that we still need a more fundamental understanding of the ionic mobilities in these compounds, and how they can be influenced by such

strategies as anion replacement and nanoconfinement. Also crucial is a better understanding of their chemical and electrochemical stabilities, most notably pertaining to their interface interactions with the positive electrode. Nevertheless, it is clear that this rapidly expanding family of complex metal hydrides with high room-temperature conductivities provides for a rather intriguing area of fundamental scientific research that can ultimately lead to exciting practical applications for these materials in next-generation, all-solid-state, lithium-ion, and other rechargeable batteries.

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References

1. J.B. Goodenough, K.S. Park, *J. Am. Chem. Soc.* **135**, 1167 (2013)
2. P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.M. Tarascon, *Nat. Mater.* **11**, 19 (2012)
3. H.G. Jung, J. Hassoun, J.B. Park, Y.K. Sun, B. Scrosati, *Nat. Chem.* **4**, 579 (2012)
4. J.M. Tarascon, *Philos. Trans. R. Soc. Math. Phys. Eng. Sci.* **368**, 3227 (2010)
5. Y. Kato, K. Kawamoto, R. Kanno, M. Hirayama, *Electrochemistry* **80**, 749 (2012)
6. S.S. Zhang, *J. Power Sources* **231**, 153 (2013)
7. A.C. Luntz, B.D. McCloskey, *Chem. Rev.* **114**, 11721 (2014)
8. Y. Oumellal, A. Rougier, G.A. Nazri, J.-M. Tarascon, L. Aymard, *Nat. Mater.* **7**, 916 (2008)
9. Y. Oumellal, C. Zlotea, S. Bastide, C. Cachet-Vivier, E. Leonel, S. Sengmany, E. Leroy, L. Aymard, J.-P. Bonnet, M. Latroche, *Nanoscale* **6**, 14459 (2014)
10. J. Zhang, W. Zaidi, V. Paul-Boncour, K. Provost, A. Michalowicz, F. Cuevas, M. Latroche, S. Belin, J.-P. Bonnet, L. Aymard, *J. Mater. Chem. A* **1**, 4706 (2013)
11. K. Provost, J. Zhang, W. Zaidi, V. Paul-Boncour, J.-P. Bonnet, F. Cuevas, S. Belin, L. Aymard, M. Latroche, *J. Phys. Chem. C* **118**, 29554 (2014)
12. J.A. Teprovich, J. Zhang, H. Colón-Mercado, F. Cuevas, B. Peters, S. Greenway, R. Zidan, M. Latroche, *J. Phys. Chem. C* **119**, 4666 (2015)
13. W. Zaidi, J.-P. Bonnet, J. Zhang, F. Cuevas, M. Latroche, S. Couillaud, J.-L. Bobet, M.T. Sougrati, J.C. Jumas, L. Aymard, *Int. J. Hydrog. Energy* **38**, 4798 (2013)
14. Y. Oumellal, W. Zaidi, J.-P. Bonnet, F. Cuevas, M. Latroche, J. Zhang, J.-L. Bobet, A. Rougier, L. Aymard, *Int. J. Hydrog. Energy* **37**, 7831 (2012)
15. L. Grande, E. Paillard, J. Hassoun, J.B. Park, Y.J. Lee, Y.K. Sun, S. Passerini, B. Scrosati, *Adv. Mater.* **27**, 784–800 (2015)
16. J.M. Tarascon, M. Armand, *Nature* **414**, 359 (2001)
17. N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, *Nat. Mater.* **10**, 682 (2011)
18. D.S. Stasinevitch, G.A. Egorenko, *Russ. J. Inorg. Chem.* **13**, 341 (1968)
19. B. Bogdanovic, M. Schwickardi, *J. Alloys Compd.* **253–254**, 1 (1997)
20. A. Züttel, S. Rentsch, P. Fischer, P. Wenger, P. Sudan, P. Mauron, C. Emmenegger, *J. Alloys Compd.* **356–357**, 515 (2003)
21. B.A. Boukamp, R.A. Huggins, *Phys. Lett. A* **72**, 464 (1979)
22. M. Matsuo, S. Orimo, *Adv. Energy Mater.* **1**, 161 (2011)
23. M. Matsuo, Y. Nakamori, S. Orimo, H. Maekawa, H. Takamura, *Appl. Phys. Lett.* **91**, 4103 (2007)
24. T. Ikeshoji, E. Tsuchida, T. Morishita, K. Ikeda, M. Matsuo, Y. Kawazoe, S. Orimo, *Phys. Rev. B* **83**, 144301 (2011)
25. J.P. Soulié, G. Renaudin, R. Erný, K. Yvon, *J. Alloys Compd.* **346**, 200 (2002)
26. P.C. Aeberhard, K. Refson, W.I.F. David, *Phys. Chem. Chem. Phys.* **15**, 8081 (2013)
27. Y. Filinchuk, D. Chernyshov, R. Cerny, *J. Phys. Chem. C* **112**, 10579 (2008)
28. A. Unemoto, M. Matsuo, S. Orimo, *Adv. Funct. Mater.* **24**, 2267 (2014)
29. J.S.G. Myrdal, D. Blanchard, D. Sveinbjörnsson, T. Vegge, *J. Phys. Chem. C* **117**, 9084 (2013)
30. V. Epp, M. Wilkening, *Phys. Rev. B* **82**, 020301 (2010)
31. A.V. Skripov, A.V. Solonin, L.H. Rude, T.R. Jensen, Y. Filinchuk, *J. Phys. Chem. C* **116**, 26177 (2012)
32. D. Sveinbjörnsson, J.S.G. Myrdal, D. Blanchard, J.J. Bentzen, T. Hirata, M.B. Mogensen, P. Norby, S. Orimo, T. Vegge, *J. Phys. Chem. C* **117**, 3249 (2013)
33. L.M. Arnbjerg, D.B. Ravnsbæk, Y. Filinchuk, R.T. Vang, Y. Cerenius, F. Besenbacher, J.E. Jørgensen, H.J. Jakobsen, T.R. Jensen, *Chem. Mater.* **21**, 5772 (2009)
34. A. Remhof, P. Mauron, A. Züttel, J.P. Embs, Z. Łodziana, A.J. Ramirez-Cuesta, P. Ngene, P. de Jongh, *J. Phys. Chem. C* **117**, 3789 (2013)
35. D.T. Shane, R.L. Corey, C. McIntosh, L.H. Rayhel, R.C. Bowman, J.J. Vajo, A.F. Gross, M.S. Conradi, *J. Phys. Chem. C* **114**, 4008 (2010)
36. X. Liu, E.H. Majzoub, V. Stavila, R.K. Bhakta, M.D. Allendorff, D.T. Shane, M.S. Conradi, N. Verdál, T.J. Udovic, S.-J. Hwang, *J. Mater. Chem. A* **1**, 9935 (2013)
37. M.H.W. Verkuijlen, P. Ngene, D.W. de Kort, C. Barré, A. Nale, E.R.H. van Eck, P.J.M. van Bentum, P.E. de Jongh, A.P.M. Kentgens, *J. Phys. Chem. C* **116**, 22169 (2012)
38. P. Ngene, P. Adelhelm, A.M. Beale, K.P. De Jong, P.E. De Jongh, *J. Phys. Chem. C* **114**, 6163 (2010)
39. D. Blanchard, A. Nale, D. Sveinbjörnsson, T.M. Eggenhuisen, M.H.W. Verkuijlen, S. Suwarno, T. Vegge, A.P.M. Kentgens, P.E. de Jongh, *Adv. Funct. Mater.* **25**, 184 (2015)
40. N. Verdál, T.J. Udovic, J.J. Rush, X. Liu, E.H. Majzoub, J.J. Vajo, A.F. Gross, *J. Phys. Chem. C* **117**, 17983 (2013)
41. F.W. Poulsen, N.H. Andersen, B. Kindl, J. Schoonman, *Solid State Ion.* **9–10**, 119 (1983)
42. V.G. Ponomareva, G.V. Lavrova, L.G. Simonova, *Solid State Ion.* **119**, 295 (1999)
43. C.C. Liang, *J. Electrochem. Soc.* **120**, 1289 (1973)
44. H. Oguchi, M. Matsuo, T. Sato, H. Takamura, H. Maekawa, H. Kuwano, S. Orimo, *J. Appl. Phys.* **107**, 6104 (2010)
45. L. Silvestri, S. Forgia, L. Farina, D. Meggiolaro, S. Panero, A. La Barbera, S. Brutti, P. Reale, *ChemElectroChem* **2**, 877 (2015)
46. M.B. Ley, S. Boulinau, R. Janot, Y. Filinchuk, T.R. Jensen, *J. Phys. Chem. C* **116**, 21267 (2012)
47. P. Hartmann, C.L. Bender, M. Vračar, A.K. Dürr, A. Garsuch, J. Janek, P. Adelhelm, *Nat. Mater.* **12**, 228 (2013)

48. M. Matsuo, S. Kuromoto, T. Sato, H. Oguchi, H. Maekawa, H. Takamura, S. Orimo, *Appl. Phys. Lett.* **100**, 203904 (2012)
49. T.J. Udovic, M. Matsuo, A. Unemoto, N. Verdal, V. Stavila, A.V. Skripov, J.J. Rush, H. Takamura, S. Orimo, *Chem. Commun.* **50**, 3750 (2014)
50. T.J. Udovic, M. Matsuo, W.S. Tang, H. Wu, V. Stavila, A.V. Soloninin, R.V. Skoryunov, O.A. Babanova, A.V. Skripov, J.J. Rush, A. Unemoto, H. Takamura, S. Orimo, *Adv. Mater.* **26**, 7622 (2014)
51. K. Takahashi, K. Hattori, T. Yamazaki, K. Takada, M. Matsuo, S. Orimo, H. Maekawa, H. Takamura, *J. Power Sources* **226**, 61 (2013)
52. D. Sveinbjörnsson, A.S. Christiansen, R. Viskinde, P. Norby, T. Vegge, *J. Electrochem. Soc.* **161**, A1432 (2014)
53. A. Unemoto, T. Ikeshoji, S. Yasaku, M. Matsuo, V. Stavila, T.J. Udovic, S. Orimo, *Chem. Mater.* **27**, 5407 (2015)
54. L. Zeng, K. Kawahito, S. Ikeda, T. Ichikawa, H. Miyaoka, Y. Kojima, *Chem. Commun.* **51**, 9773 (2015)